Lipid Composition of Natural Rubber Sheet and Relationship with its Structure and Properties

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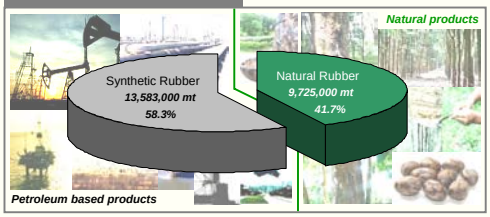
1. Present situation of natural rubber

WORLD ELASTOMER MARKET

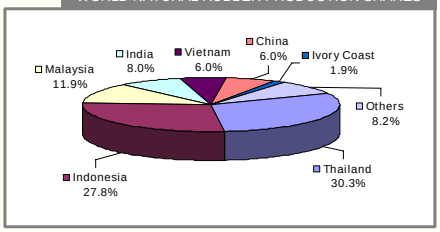


In year 2007, total production of natural rubber over the world stood at about 9.73 million tons all over the world (IRSG, 2008). Thanks to certain unequalled properties, natural rubber (NR) keeps its share in world elastomer market with around 40% for more than 15 years.

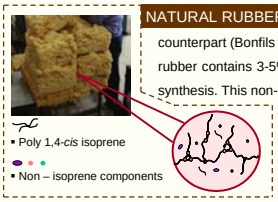
Presently, around 93% of the world production comes from Asia as shown in the figure, the major producers being Thailand (32.5%), Indonesia (27.3%), Malaysia (13.3%) and India (8.8%).

For Thailand, the exported NR products are block rubber (37% of exported products and mainly STR20), rubber sheets (33%, mainly RSS3) and concentrated latex (30%, mainly HA and LATZ) (Thai Ministry of Commerce, 2008).

WORLD NATURAL RUBBER PRODUCTION SHARES



2. natural rubber structure and properties

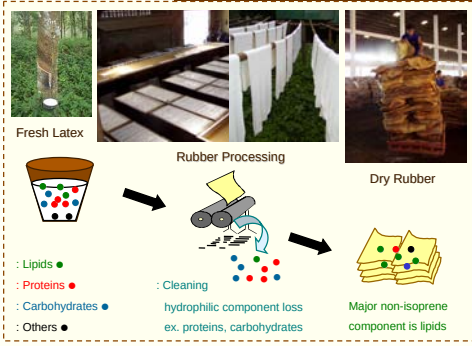


NATURAL RUBBER STRUCTURE is more complicated than the one of its synthetic counterpart (Bonfils and Vaysse, 2003). Apart from its 100% *cis*-configuration polyisoprene, natural rubber contains 3-5% of non-isoprene component, a part that could not be mimicked by chemical synthesis. This non-rubber fraction has been suspected to be responsible for both superior properties and inconsistent quality of natural rubber.

Variability of natural rubber properties such as initial plasticity (P_0) or plasticity retention index (PRI) are indeed not appreciated by second transformation industry which use more and more automated processes.

During raw natural rubber processing, some of non-isoprene components are lost with water used during cleaning process while others, especially lipids are retained in dry rubber due to their hydrophobic properties.

FROM FRESH LATEX TO DRY RUBBER



3. Research question

Lipids have been described to play roles on some rubber properties in both raw and vulcanized states. Unfortunately, obtained results are hardly comparable due to the difference of rubber sources, method of extraction and analytical techniques. Only one comprehensive work dealing with the eventual relationships between lipid composition and the lack of consistency of natural rubber properties has been published (Hasma, 1984).

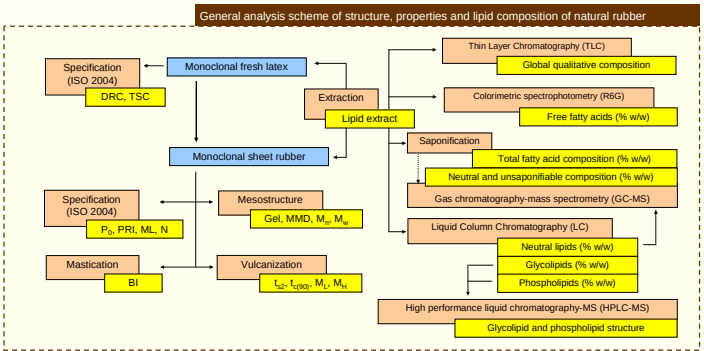
Our research question was :

"IS LIPID COMPOSITION RELATED TO THE LACK OF CONSISTENCY OF NATURAL RUBBER PROPERTIES?"

4. Methodology

The samplings were carried out in the plantation of Visahakit Thai Rubber Co.,LTD in Chantaburi province, Thailand. Four popular rubber clones were chosen: RRIM600, GT1, BPM24 and PB235. Unsmoked sheet (USS) which was proved to be similar as ribbed smoked sheet (RSS) in terms of properties (Rodphakdeekul *et. al,* 2008) was used as dry rubber model. Lipids from fresh latex and dry rubber were extracted after methodological optimization (Liengprayoon *et. al,* 2008). The analyses performed for each sample are presented in the scheme below.

General analysis scheme of structure, properties and lipid composition of natural rubber



5. Lipid composition of natural rubber

Lipids from fresh latex from four *H. brasiliensis* clones were characterized and found to be clonal dependent (2.5 – 3.7% w/w dry rubber). PB235 clone was the highest lipid containing clone followed by BPM24, RRIM600 and GT1. The amount of lipids in USS was found to be lower (2.0 – 3.3%) than in latex but the ranking remained the same. Comparison of lipid classes between fresh latex and USS revealed that the quantity of polar lipids in USS decreased by around 50% for glycolipids and 80% for phospholipids from their initial quantity in latex. This change could be due to enzyme-catalyzed hydrolysis as lipase activity was observed in fresh latex. However, the clonal specificity of lipid profile observed in fresh latex remained unchanged in the corresponding sheet rubber.

Lipid composition of natural rubber latex and its corresponding sheet rubber

1. Fresh latex

- **Lipids : 2.5 – 3.7% (w/w dry rubber)**
  - Neutral lipids: 39 - 61% (w/w total lipids)
  - Glycolipids: 21 - 36% (w/w total lipids)
  - Phospholipids: 18 - 26% (w/w total lipids)
- **Free fatty acids : 0.04 – 0.06% (w/w dry rubber)**
- **Total fatty acids : 0.8 – 2.0% (w/w dry rubber)**
  - C18:2: 37 - 53% (RRIM600, GT1 and BPM24)
  - Furan fatty acid: 74% (PB235)
- **Unsaponifiable : 0.9 – 1.6% (w/w dry rubber)**
  - β-sitosterol: 34 - 46% (w/w total unsaponifiable)
  - Δ^5-avenasterol was identified

2. Unsmoked sheet (USS)

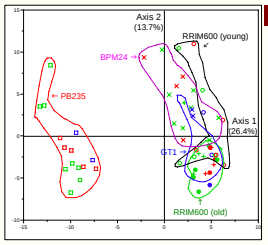
- **Lipids : 2.0 – 3.3% (w/w dry rubber)**
  - Neutral lipids: 82 - 86% (w/w total lipids)
  - Glycolipids: 10 - 13% (w/w total lipids)
  - Phospholipids: 4 - 5% (w/w total lipids)
- **Free fatty acids : 0.4 – 0.6% (w/w dry rubber)**
- **Total fatty acids : 0.9 – 1.9% (w/w dry rubber)**
  - C18:2: 33 - 44% (RRIM600, GT1 and BPM24)
  - Furan fatty acid: 81% (PB235)
- **Unsaponifiable : 0.9 – 1.1% (w/w dry rubber)**
  - β-sitosterol: 40 - 59% (w/w total unsaponifiable)
  - Δ^5-avenasterol was identified

From various chromatographic analyses, precise structural information could be obtained. Furan fatty acid (FFA) clearly distinguished PB235 from the other clones as this atypical fatty acid represented more than 70% of its total fatty acid content, while linoleic acid (C18:2) was the main fatty acid in the other clones. Among the detected compounds in unsaponifiable fraction, β-sitosterol was the major sterol in every clone. Moreover, the presence of Δ^5-avenasterol which was previously claimed to be fucosterol was proved in this study. The structural analysis of fresh latex polar lipids using HPLC/ESI-MS showed that both FFA and Δ^5-avenasterol were more present in neutral lipids and glycolipids than in phospholipids for every clone even in PB235.

In parallel with lipid analysis, USS samples were characterized for their structures and properties in order to identify possible correlations.

6. Relationship between lipid composition, structures and properties of NR

The variability of the collected data from 15 samplings (April 2004 – December 2006) i.e. lipid composition, natural rubber structure (molar mass distribution and gel content) and properties (P_0, PRI, breakdown and vulcanization behavior) was represented using principle component analysis (PCA) as shown in figure below.



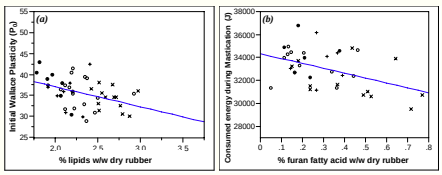
Variables

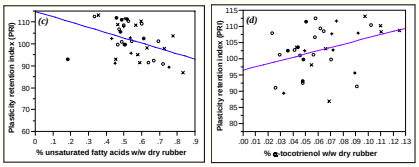
- Clones (4)
- Season (3)
- Ages (2)
- Lipid composition (98)
- Mesostructure (7)
- Macrostructure (6)
- Breakdown behavior (12)
- Vulcanization characteristics (20)

Principal component analysis showed clearly that data from PB235 clone play an important role in the global variance of obtained data. Indeed, in most cases, PB235 clone displayed distinguishable characteristics. To get rid of unknown (or not lipid-dependent) PB235 clonal effect, correlations were therefore observed by putting PB235 apart from the others namely RRIM600 (old and young), GT1 and BPM24.

From further pair correlation determined by analysis of variance with an observed significance probability less than 0.05 ($P \leq 0.05$), lipids was found to correlate with various natural rubber structures and properties. Some examples are illustrated below.

Negative correlation between P_0 and total lipids, neutral lipids and fatty acids *(a)* especially esterified form of furan fatty acid which indicated a plasticizing effect of lipids. This effect resulted in the drop of consumed energy during mastication assessed by Breakdown Index method *(b)*.





Negative correlation between PRI and fatty acids especially unsaturated fatty acids indicated the activity of such fatty acids as prooxidant *(c)*. α-tocotrienol and stigmasterol were found to act as antioxidant in every studied clone (d).

7. Conclusions and perspectives

This study permitted a characterization of lipids composition, structures and properties of fully identified natural rubber samples from various *Hevea* clones, collected in a database. This allowed through statistical analyses, to provide an overview of the relationships between lipid composition and natural rubber properties. It can be seen that lipids display both advantage and disadvantage effects on natural rubber properties. Some involvements with structure of natural rubber have been also mentioned. Moreover, USS rubber displayed a high but narrow range. With the knowledge from this work, further studies are in progress using a similar approach with various rubber types whose properties cover a wider range of values.

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Acknowledgement: Author wish to thank French-Thai committee project, and Thailand Research Fund (TRF) for their financial support and also Visahakit Thai Rubber for samples providing and the hosting of field experiment .